Heyrovský - Ilkovič Lecture 2024

Perspective electrochemical sensors based on biochar material

prof. Ing. Ľubomír Švorc, DrSc.

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FACULTY OF CHEMICAL AND FOOD TECHNOLOGY

SLOVENSKÁ CHEMICKÁ SPOLOČNOSŤ
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EuChemS
European Chemical Society
Division of Analytical Chemistry

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Current state in analytical chemistry

- **Goal and trends:** increase demands on analytical laboratories (implementation of new decrees and laws in practice)

- **Requirements:** implementation of new trends in green chemistry in the development and validation of advanced analytical methods, procedures and tools as an *alternative to conventional and routine methods* specified in standards and regulations

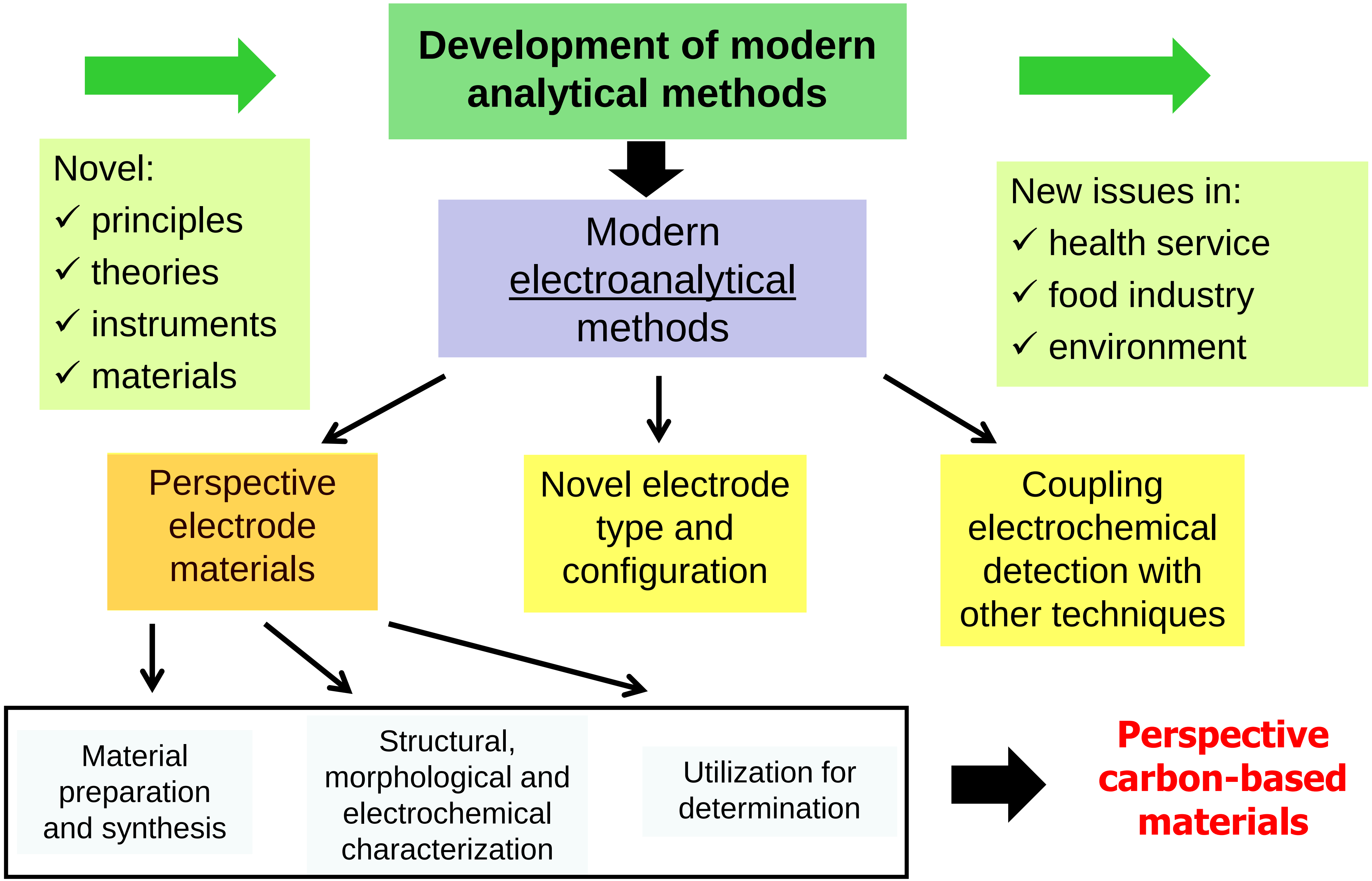
- ***The concept of Green Analytical Chemistry***

- **Criteria:**
  - simplicity and speed
  - sensitivity, selectivity, reliability, robustness
  - miniaturization and portability

- **Important aspect:** competitiveness of analytical methods in terms of aspects:
  - economic: availability, price
  - analytical: method performance - validation parameters
  - practical: time-saving

- **Development and use of new and "green" materials in (analytical) chemistry**

Current trends in electroanalytical chemistry



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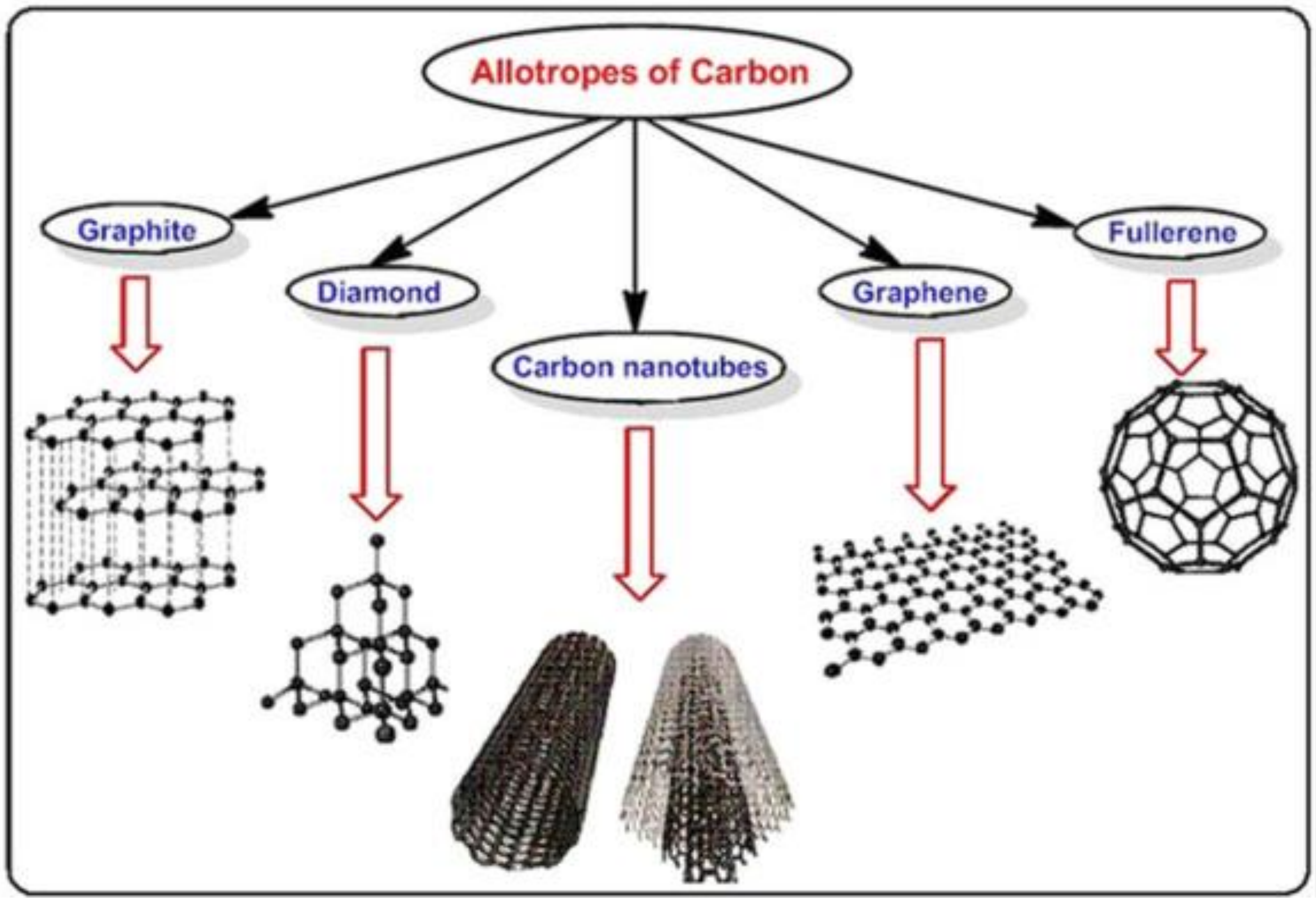
Carbonaceous materials



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What is biochar?

- carbon-rich material (50-95%) produced by thermal degradation of biomass at relatively low temperatures (300-800 °C) without the presence or with limited oxygen access

- low CO_2 emissions (1 ton of biochar can captive 2.5-3 tons of CO_2) and the use of pyrolysis by-products as raw materials → **green and cheaper alternative to traditional adsorbents** such as activated carbon

Basic characteristics of biochar:

- high adsorption capacity → use in the removal of micropollutants from water (heavy metals, salts, drugs and their metabolites)

- sufficiently large surface area and porosity

- surface functionalization by different groups

- price*: 1 kg of biochar ~ 2,7 USD versus 1 kg of activated carbon ~ 20-22 USD

*Ahmed *et al*.: *Biomass Bioenergy* **84**, 76-86 (2016).

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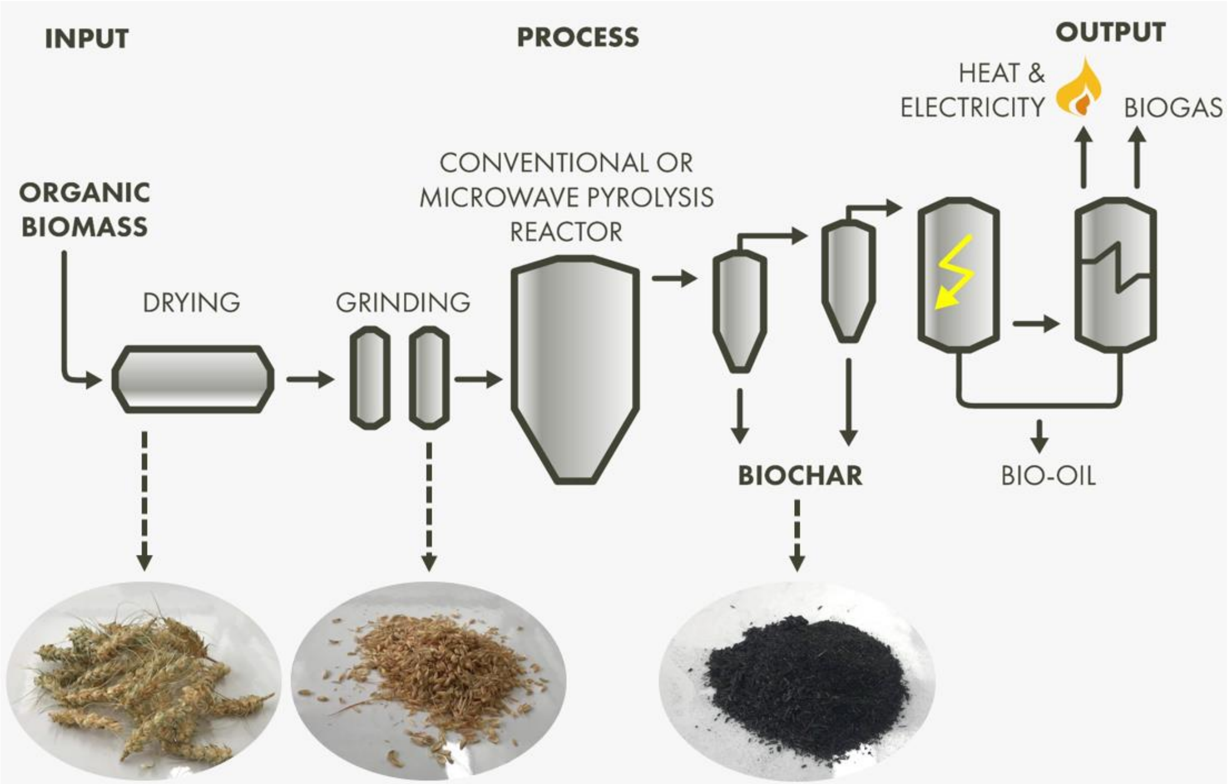
Biochar - production

Method	Temperature °C	Heating rate °C/s	Duration	Yields %
Slow pyrolysis	300-600	0.01–2	Days	**35-45 biochar** 25-35 bio-oil 20-30 syngas
Fast pyrolysis	> 600	> 2	~ 1 s	60 bio-oil **20 biochar** 20 syngas

Slow pyrolysis → reduced particle size, carboxylic and hydroxyl groups

Fast pyrolysis → coarse particles and dominant aromatic groups



Biochar – definition according to IUPAC

DE GRUYTER Pure Appl. Chem. 2024; 96(11): 1541–1572

IUPAC Technical Report

Fotis Bilias, Divine Damertey Sewu, Seung Han Woo, Ioannis Anastopoulos, Frank Verheijen, Johannes Lehmann, Wenceslau Geraldes Teixeira, Dionisios Gasparatos, Kathleen Draper and Dimitrios Kalderis*

Glossary of terms used in biochar research (IUPAC Technical Report)

https://doi.org/10.1515/pac-2021-0106
Received January 4, 2022; accepted May 22, 2024

25. **biochar**

A solid, multi-functional, porous carbonaceous product of agricultural *biomass pyrolysis* in the temperature range of 350 to 1000 °C in the absence of or under limited oxygen. The initial feedstock properties and processing conditions (heating rate, final pyrolysis temperature, residence time, *pyrolysis* equipment type) largely control the yield and physicochemical properties of *biochar*. The hydrogen-to-organic carbon (H/C_{org}) and oxygen-to-organic carbon (O/C_{org}) ratios of the as-prepared *biochar* should be below 0.7 and below 0.4, respectively. *Biochar* is used in a wide range of applications, including but not limited to soil conditioning and remediation, anaerobic digestion of organic wastes, composting, potable water and wastewater treatment, as an additive to animal feed and in composite building materials.

IUPAC Chemistry and the Environment Division (Division VI)

https://www.degruyter.com/document/doi/10.1515/pac-2021-0106/html

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Use of biochar

- in agricultural land
- in forestry
- as fodder
- in compost
- as a sorbent
- in urban areas
- in ANALYTICAL CHEMISTRY

↓

Electroanalytical chemistry?

↓

Biochar as a nontraditional and "green" electrode material for electrochemical sensors






V4 Biochar Platform: https://v4biochar.czu.cz/cs

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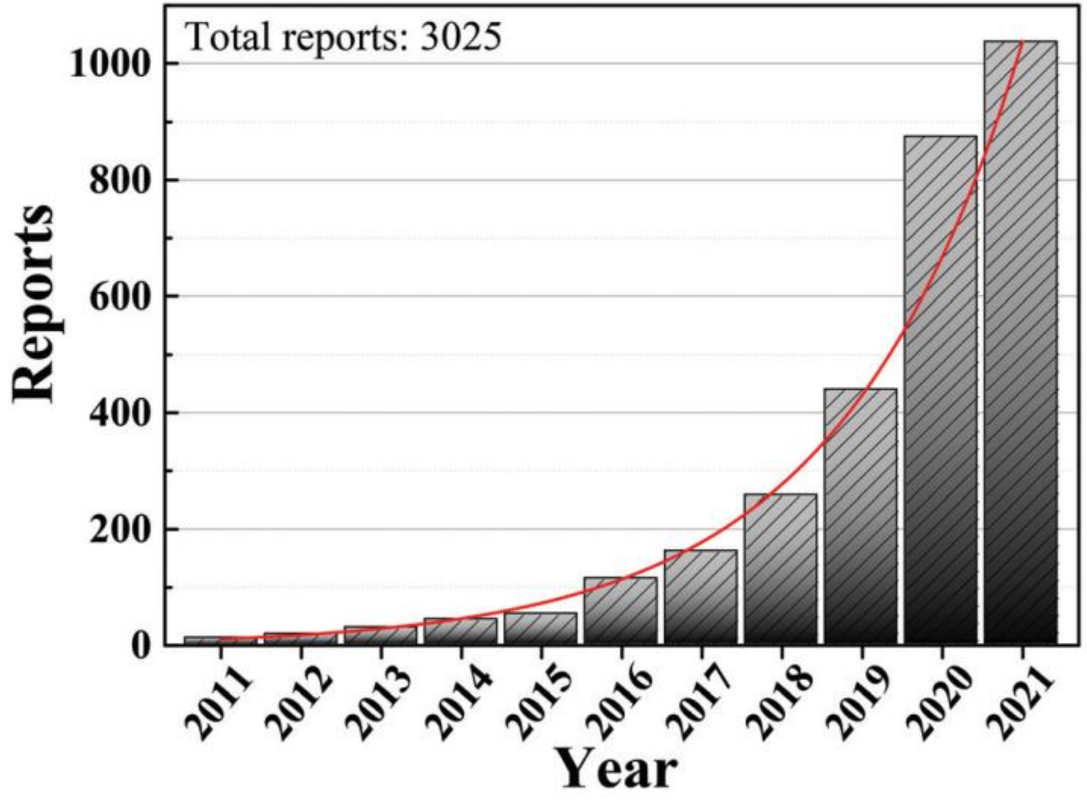
Biochar in electrochemical sensing - overview



Biochar electrochemical application research through the years. Search of WoS with the keywords "*biochar electrochemical application*".

Kalinke *et al*.: *Green Chem.* **23**, 5272 (2021).

BIOCHAR IN ELECTROANALYSIS:

Spanu *et al.*:
Biochar as an alternative sustainable platform for sensing applications: A review,
Microchem. J. **159**, 105506 (2020).

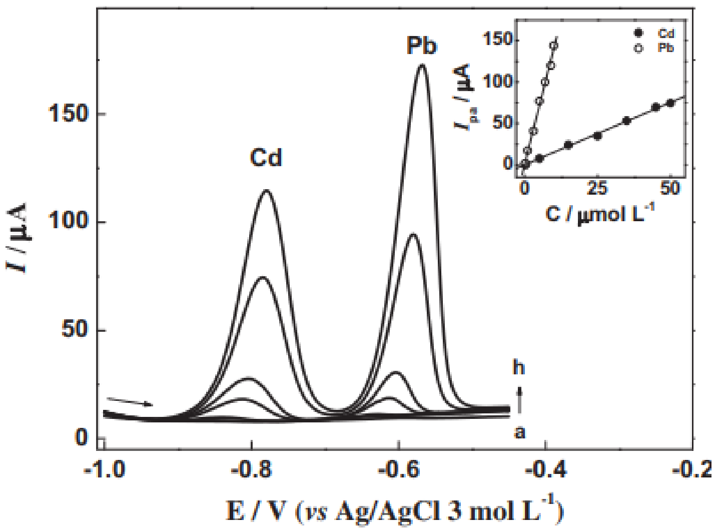
de Almeida *et al.*:
Electrochemical devices obtained from biochar: Advances in renewable and environmentally-friendly technologies applied to analytical chemistry,
Trends Environ. Anal. Chem. Chemistry **26**, e00089 (2020).

Kalinke *et al*.:
State-of-the-art and perspectives in the use of biochar for electrochemical and electroanalytical applications,
Green Chem. **23**, 5272 (2021).

Cancelliere *et al.*:
Biochar: A sustainable alternative in the development of electrochemical printed platforms,
Chemosensors **10**, 344 (2022).

Role of biochar in electrochemical sensing

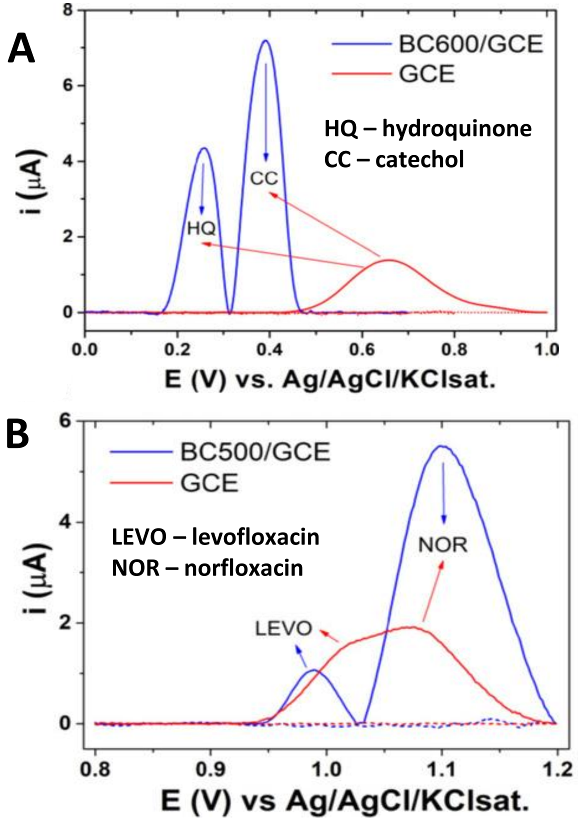
✓ **adsorbent**



DPAdSV records of Cd(II) and Pb(II) with different concentrations at CPE modified with 25% biochar in PBS (pH 5) after preconcentration by 1200 s.

Suguihiro *et al.*:
***Bioresour. Technol.* 143, 40-45 (2013).**

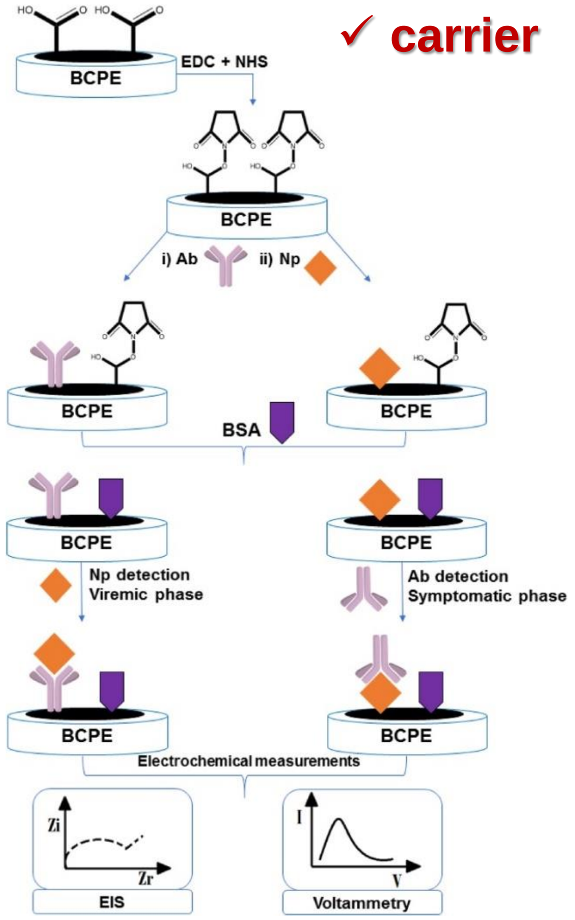
✓ **catalyst**



SWV curves obtained on a BC/GCE and GCE in the presence of:
A) HQ and CC;
B) LEVO and NOR (10 µM each).

Ferreira *et al.*:
***Electroanalysis* 30, 2233-2236 (2018).**

✓ **carrier**



Immunosensor for hantavirus (i) antibodies (Ab) or (ii) nucleoprotein (Np) detection in viremic or symptomatic phases.

Martins *et al.*:
***Talanta* 204, 163-171 (2019).**

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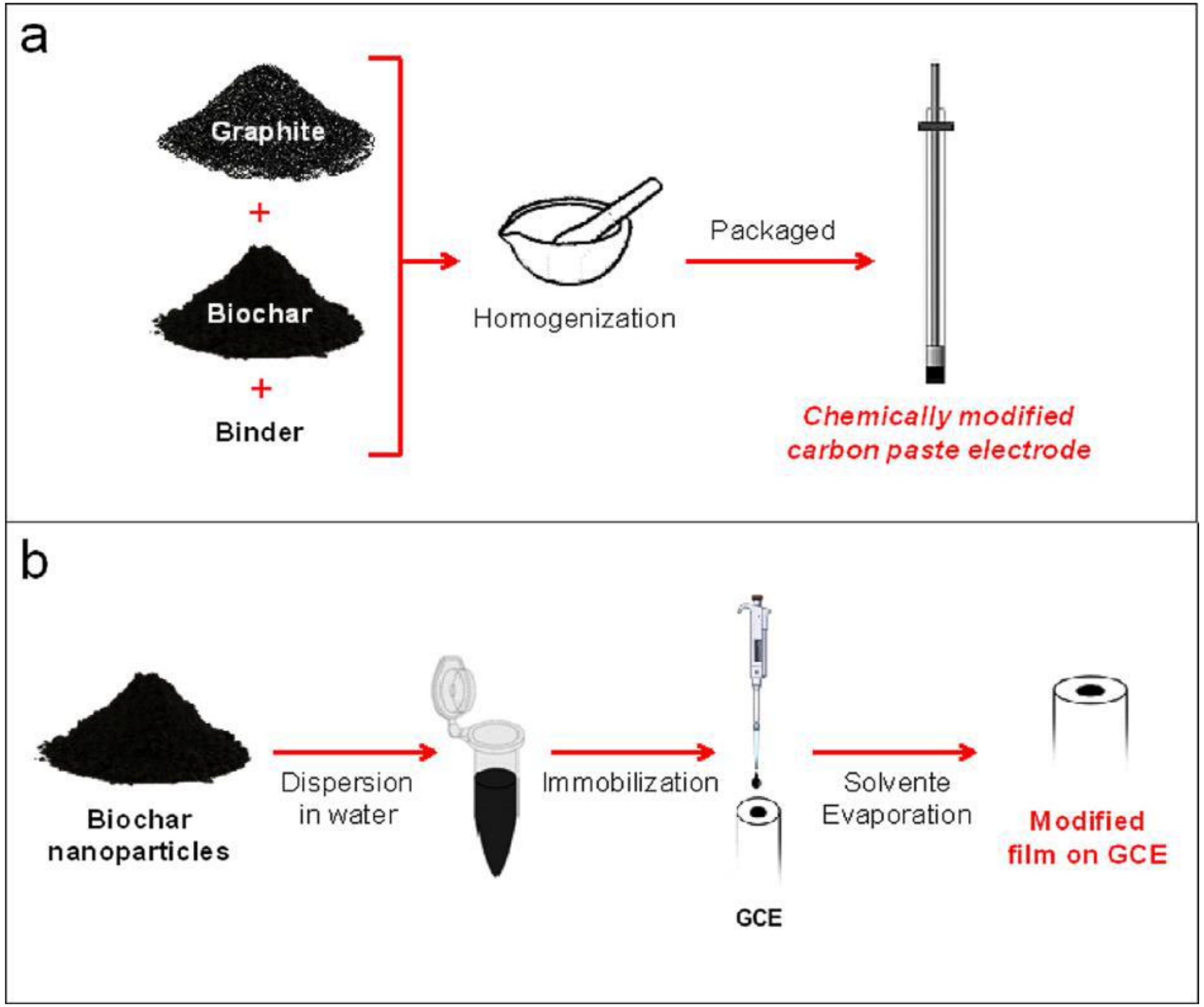
Basic configurations of biochar modification



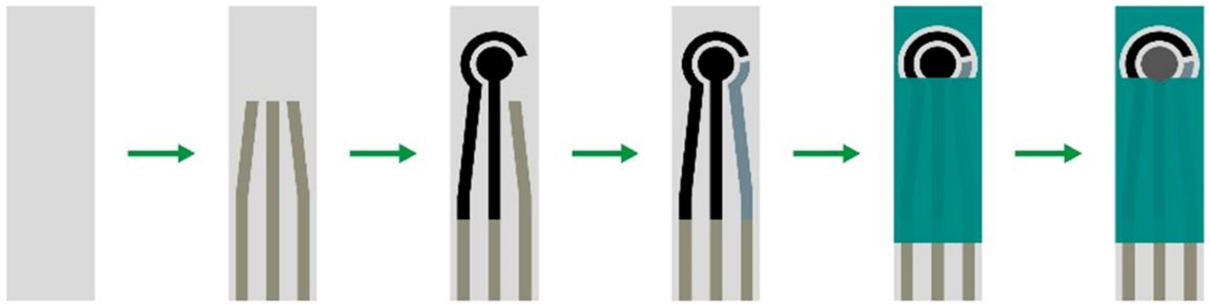
Scheme of biochar modification for **(a)** CPE and **(b)** GCE.

De Almeida *et al*.: *Trends Environ. Anal. Chem.* **26**, e00089 (2020).

Screen-printed biochar-based electrochemical sensors: fabrication, characterization and application

Institute of Analytical Chemistry
and
Department of Graphic Arts Technology and Applied Photochemistry

Švorc *et al*.: A new generation of fully-printed electrochemical sensors based on biochar/ethylcellulose-modified carbon electrodes: Fabrication, characterization and application in electroanalysis; *Electrochim. Acta* **487**, 144161 (2024).
DOI:10.1016/j.electacta.2024.1441



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Biochar powder production

- **biochar powder** – batch 4073 (Biouhel Ltd., Zlín, Czech Republic, PV 2016-555)
- pyrolysis product of digestate containing 40% corn and 60% wood silage
- pyrolysis took place at 470 °C for 25 min
- grinding of biochar on a high-speed spiral mill for 2.5 h

Elemental composition of biochar:

Batch	Ash (%)	C_{tot} (%)	C_{org} (%)	N (%)	H (%)	S (%)	O (%)	Molar ratio	
								H / C_{org}	O / C_{org}
4073	11.0	84.3	84.0	0.2	0.7	-	4.0	0.10	0.04

- high content of C_{org} (84%) →
  higher class of biochar according to *International Biochar Initiative (IBI)*

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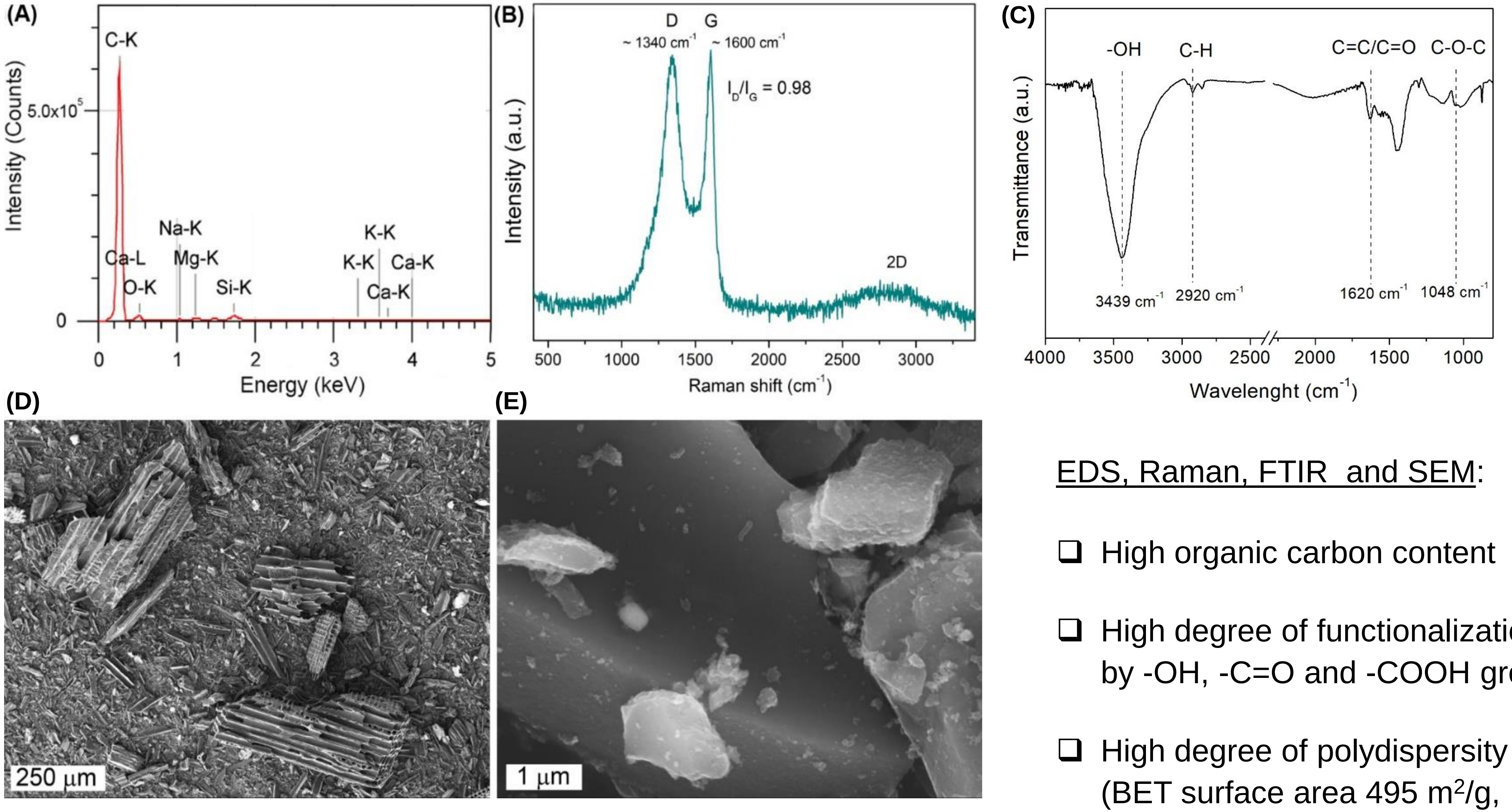
Structural and morphological characterization



(A) EDS record for elemental analysis of biochar powder.
(B) Raman spectra of biochar powder.
(C) FTIR transmittance spectra of biochar powder.
(D), (E) SEM images of biochar powder after pyrolysis.

<u>EDS, Raman, FTIR and SEM</u>:

- High organic carbon content
- High degree of functionalization by -OH, -C=O and -COOH groups
- High degree of polydispersity (BET surface area 495 m^2/g, mean particle size 90 µm)

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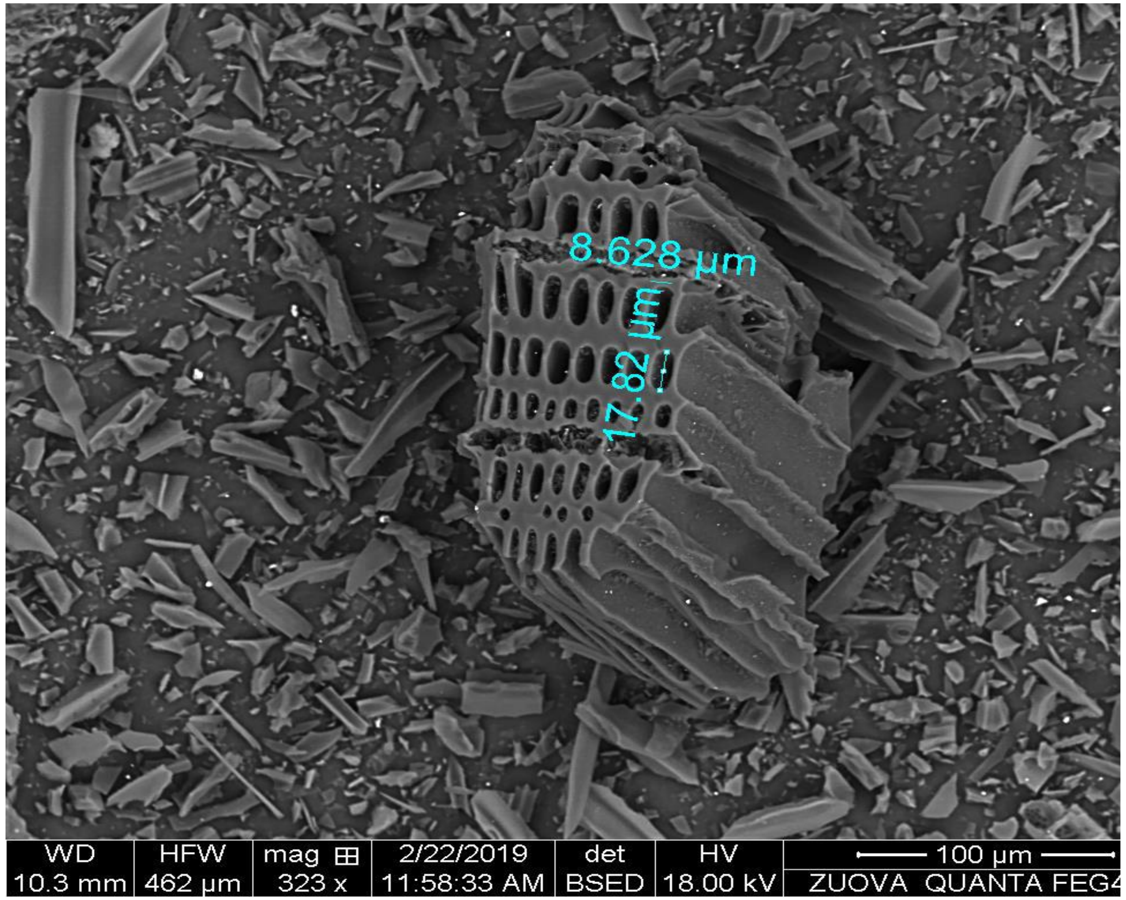
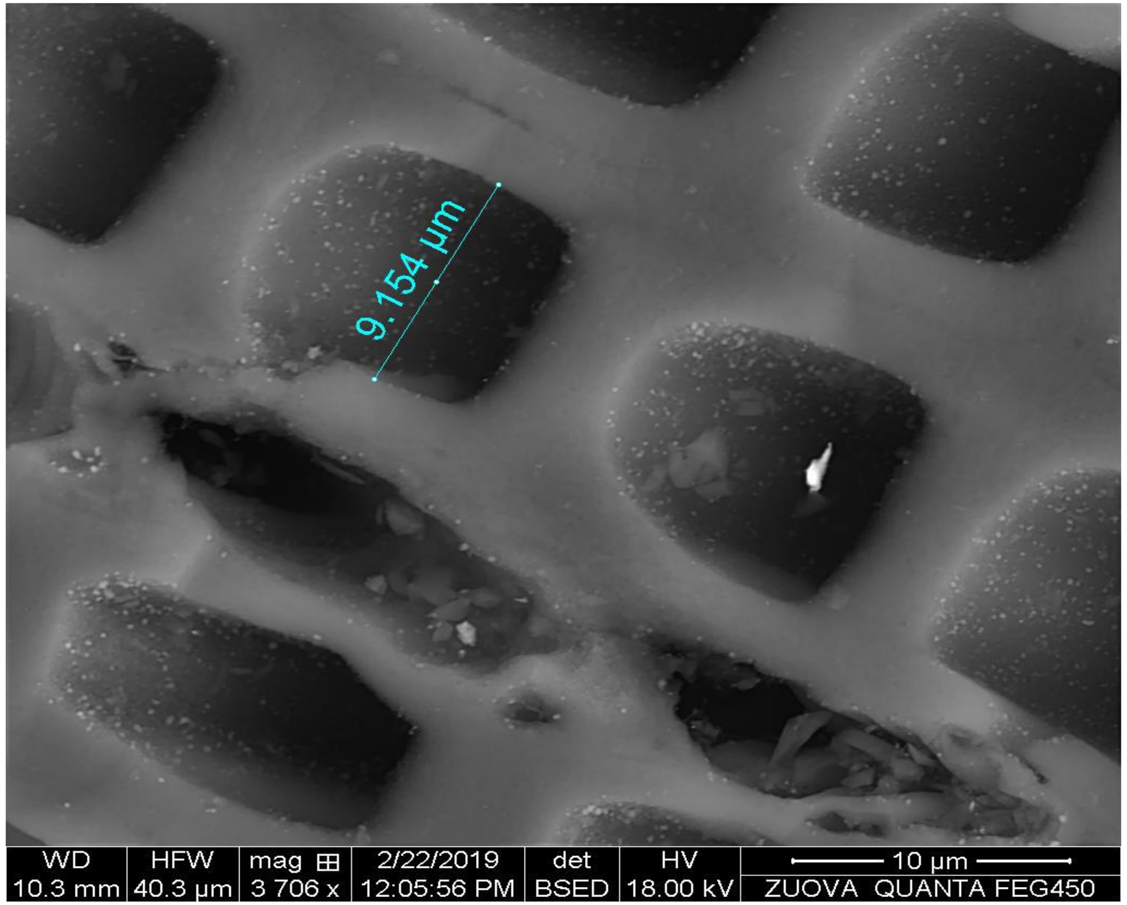
Morphological characteristics of biochar





SEM images of biochar
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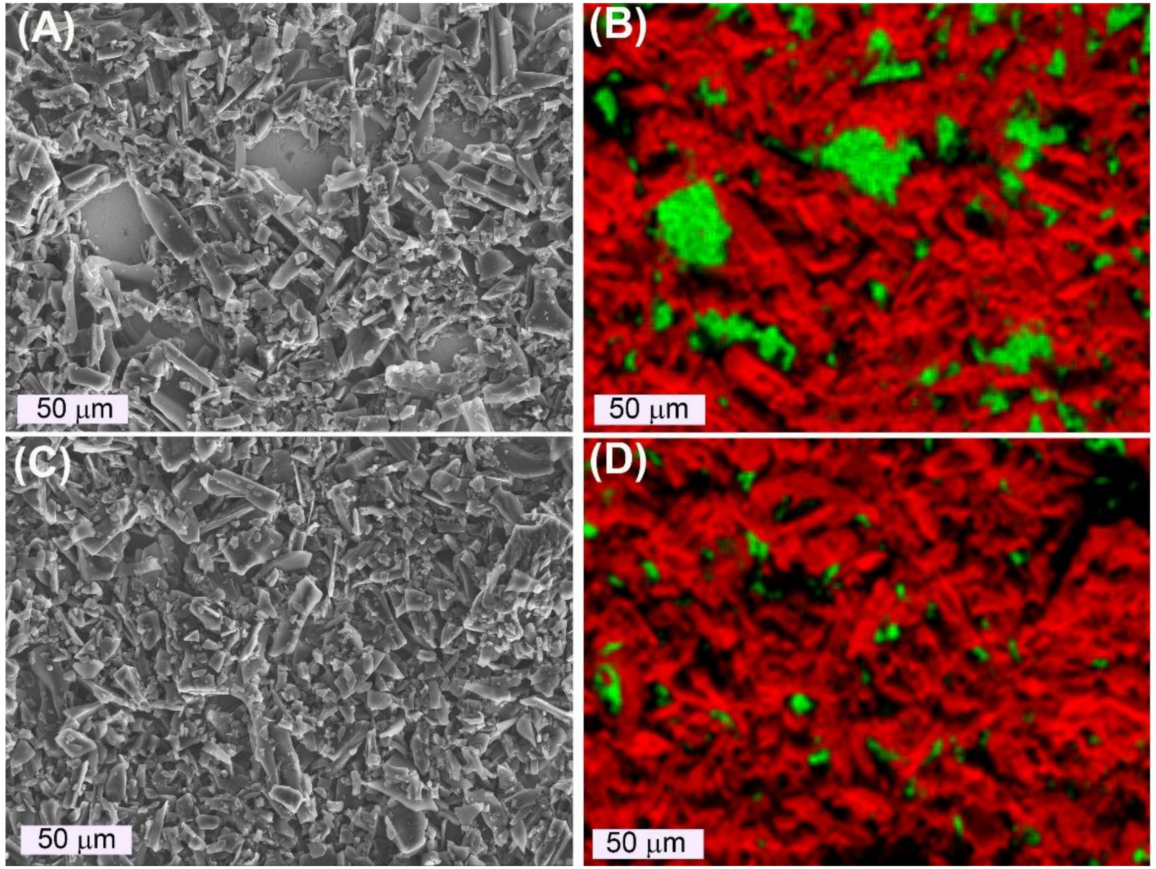
Preparation of biochar inks for screen-printing

Two steps:

I. Preparation of polymeric binder – dissolving of ethylcellulose (EC; 2-12 wt%) in terpineol

II. Preparation of biochar/EC inks – dispersing 30 wt% of biochar powder in polymeric binder (homogenized in "homemade" hand-held mixing unit)



SEM images of samples:
(A) B_EC**4**,
(C) B_EC**10**.

EDS maps of samples:
(B) B_EC**4**,
(D) B_EC**10**.

Sn signal – **green colour** (from FTO substrate)
C signal – **red colour**

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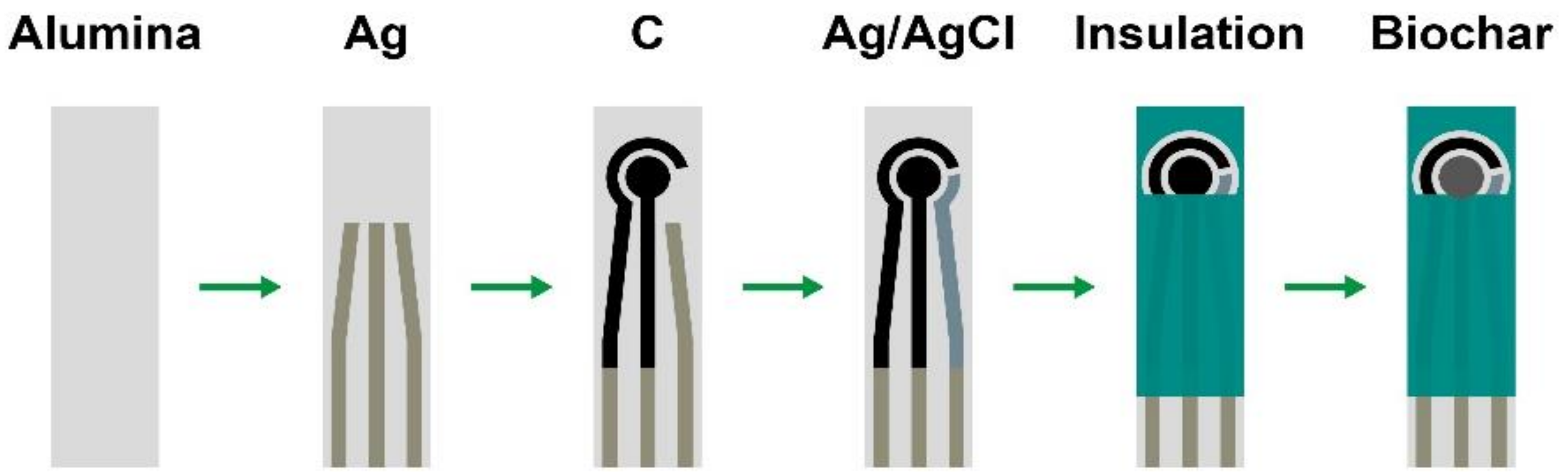
Screen-printed biochar-based electrodes

- preparation of screen-printed three-electrode systems with **working electrode** made of:

1. bare biochar electrode (B-WE)
2. bare graphite electrode (C-WE)
3. biochar-modified graphite electrode (BC-WE)

Ag/AgCl pseudoreference electrode
Graphite counter electrode



The additive production of screen-printed three-electrode electrochemical sensors with biochar/ethylcellulose working electrode.

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Švorc *et al*.: A new generation of fully-printed electrochemical sensors based on biochar/ethylcellulose-modified carbon electrodes: Fabrication, characterization and application in electroanalysis; *Electrochim. Acta* **487**, 144161 (2024). DOI:10.1016/j.electacta.2024.1441

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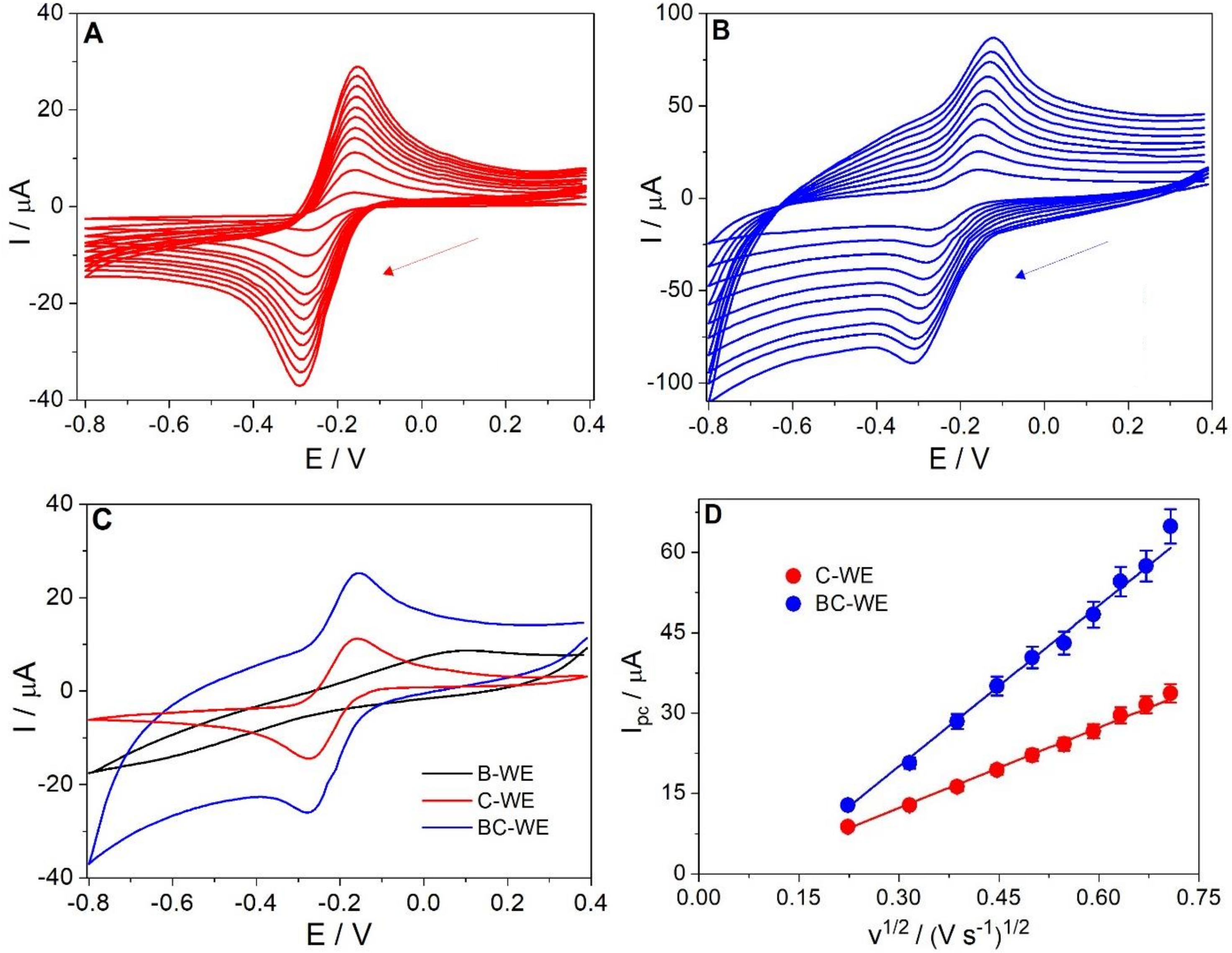
Electrochemical characterization



CV records for $[Ru(NH_3)_6]^{3+/2+}$ in 0.1 M KCl for scan rates from 0.05 to 0.5 V/s at:

(A) bare graphite
(B) biochar/graphite
(C) bare graphite, bare biochar and biochar/graphite (at 100 mV/s)
(D) bare graphite and biochar/graphite (R-S equation – calculation of area „A“)

For both working electrodes:

I_{pa}/I_{pc} ~ (0.93 - 1.00)

ΔE_p = (130-140) mV

bare graphite: I_{pc} (µA) = −2.7 + **50.0** × $v^{1/2}$ (V/s) R^2 = 0.9969 → **$A_{C\text{-}WE}$ = 0.064 cm²**

biochar-modified graphite: I_{pc} (µA) = −5.9 + **101.0** × $v^{1/2}$ (V/s) R^2 = 0.9955 → **$A_{BC\text{-}WE}$ = 0.128 cm²**

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Application of biochar-based electrochemical sensors in pharmaceutical analysis

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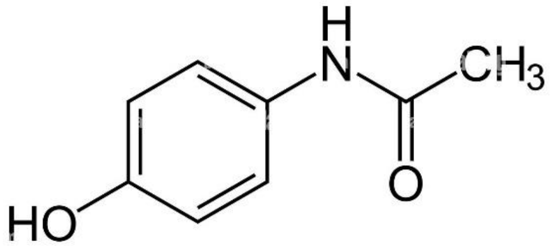
DOI:10.1016/j.electacta.2024.1441



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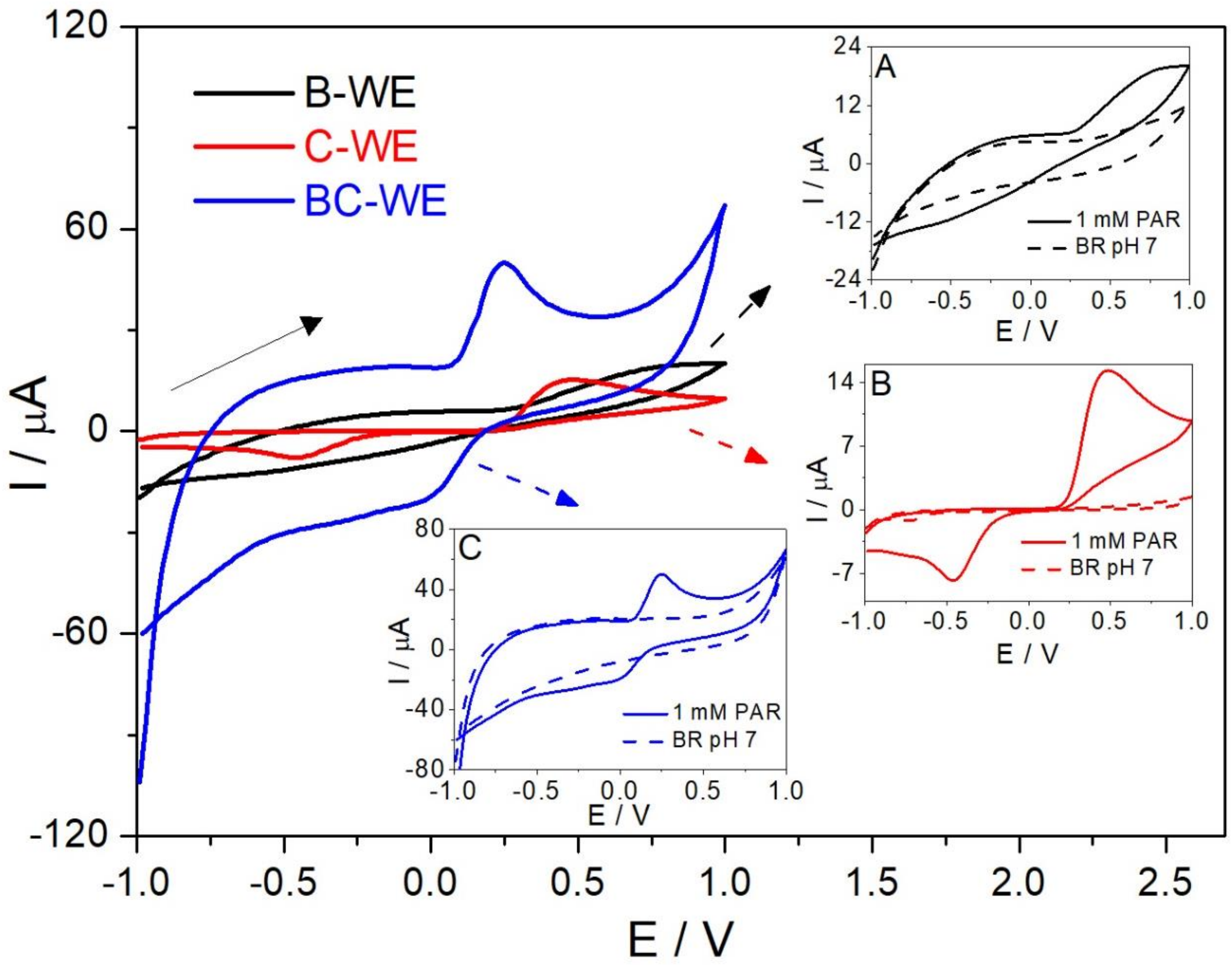
Electrochemical behaviour of paracetamol (PAR)



CV records of 1 mM PAR in BR buffer pH 7 from –1.0 V to +1.0 V with scan rate of 100 mV/s at **(A) B-WE**, **(B) C-WE** and **(C) BC-WE**.

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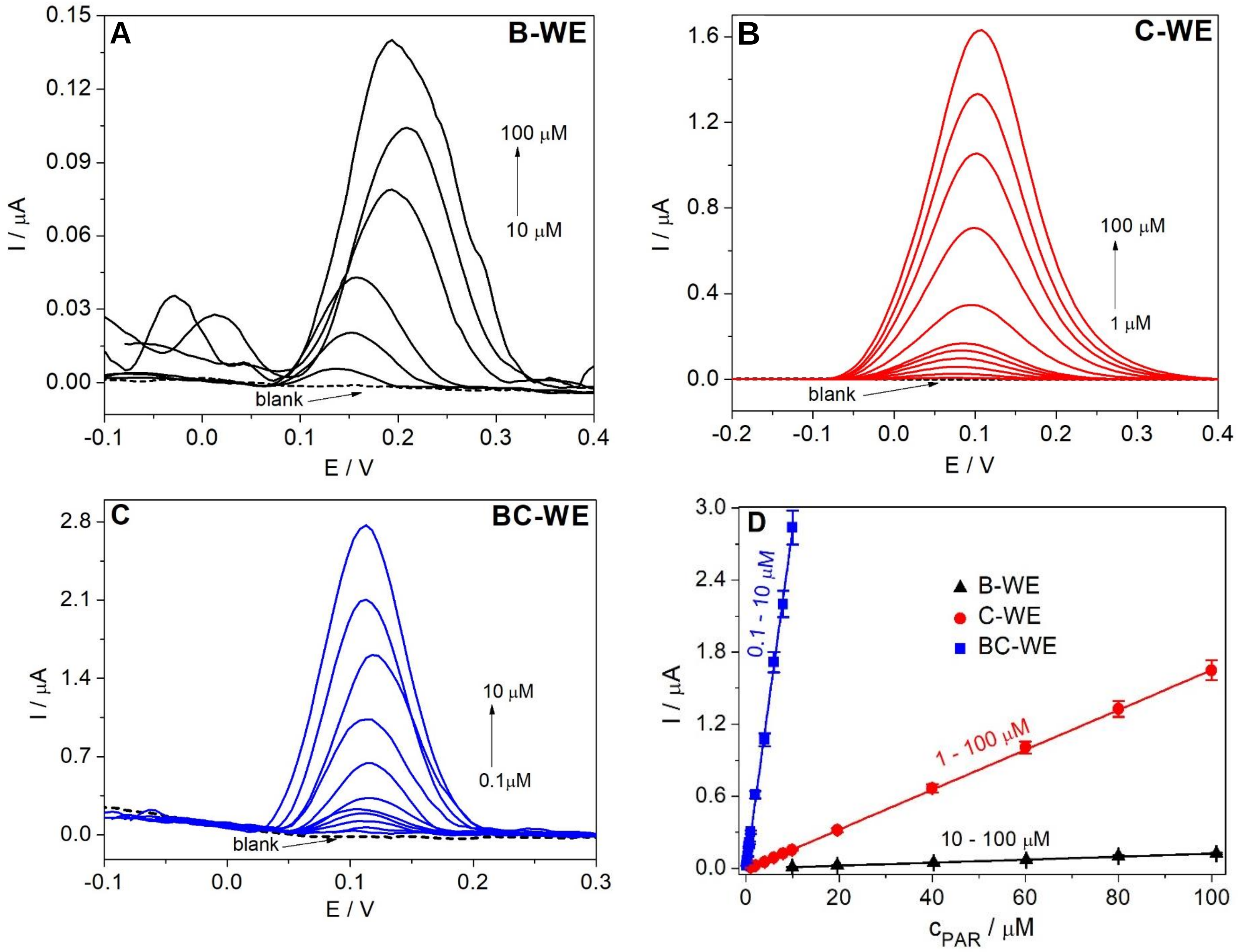
Determination of PAR using DPV



DPAdSV records for various PAR concentrations in BR buffer pH 7 at:
(A) B-WE,
(B) C-WE,
(C) BC-WE,
(D) calibration graphs.

<u>Operating parameters</u>: modulation time 100 ms, modulation amplitude 100 mV, step potential 5 mV, accumulation potential 0 V, accumulation time 300 s

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Analytical performance evaluation for PAR determination

Analytical parameter	Working electrode material of screen-printed sensor		
	Biochar (B-WE)	**Graphite (C-WE)**	**Biochar-modified graphite (BC-WE)**
Intercept ± SD (nA)	-3 ± 1	-10 ± 2	-7 ± 2
Slope ± SD (nA/μM)	1 ± 0.05	17 ± 0.1	280 ± 7
Linear concentration range (μM)	10 – 100	1 – 100	0.1 – 10
R^2	0.9906	0.9993	0.9938
LOD (μM)	3	0.4	0.02
Repeatability* (%)	7.5	3.4	4.8

***RSD for 7 consecutive DPV measurements for 5 μM PAR (**BC-WE**) and 40 μM PAR (**B-WE, C-WE**) in BR buffer pH 7

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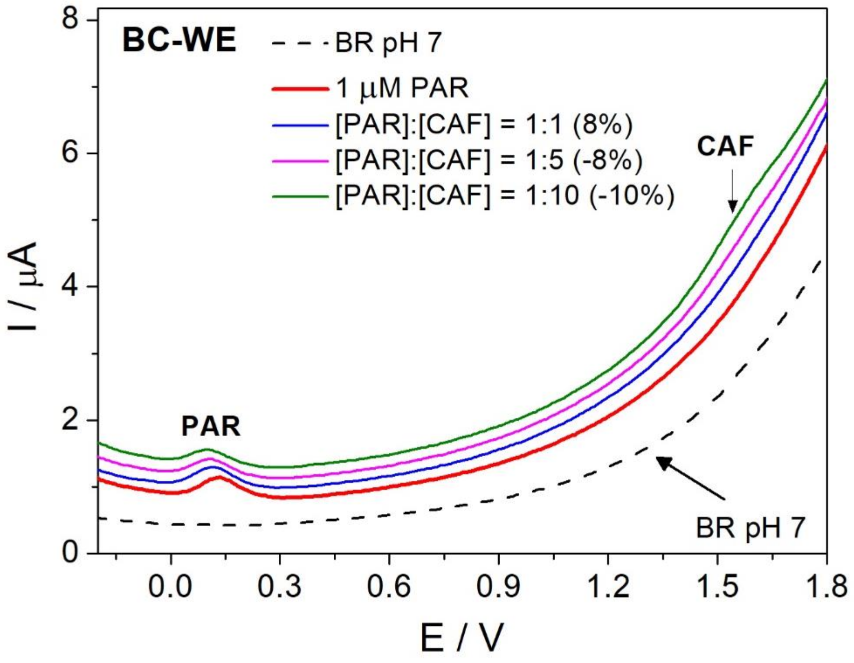
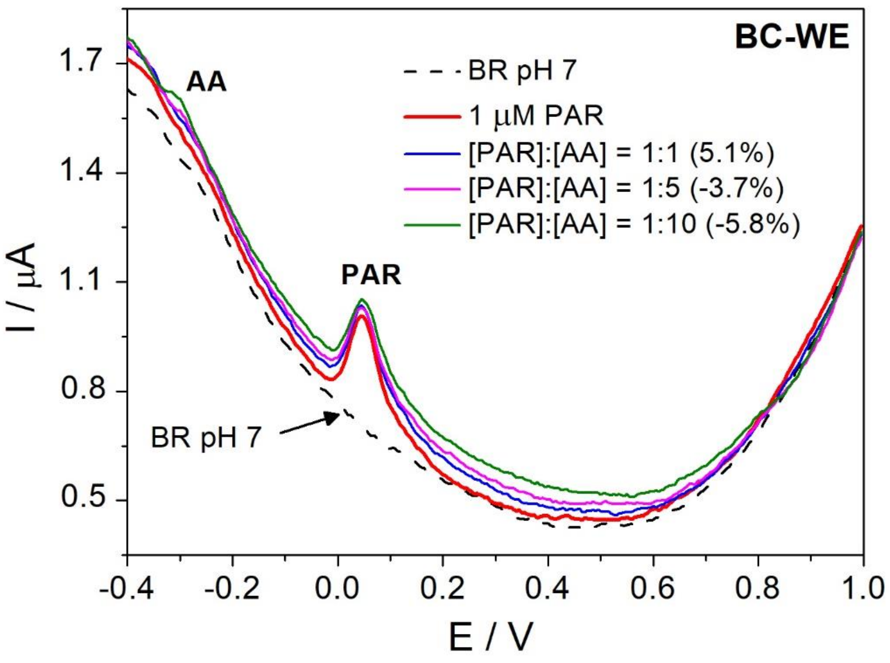
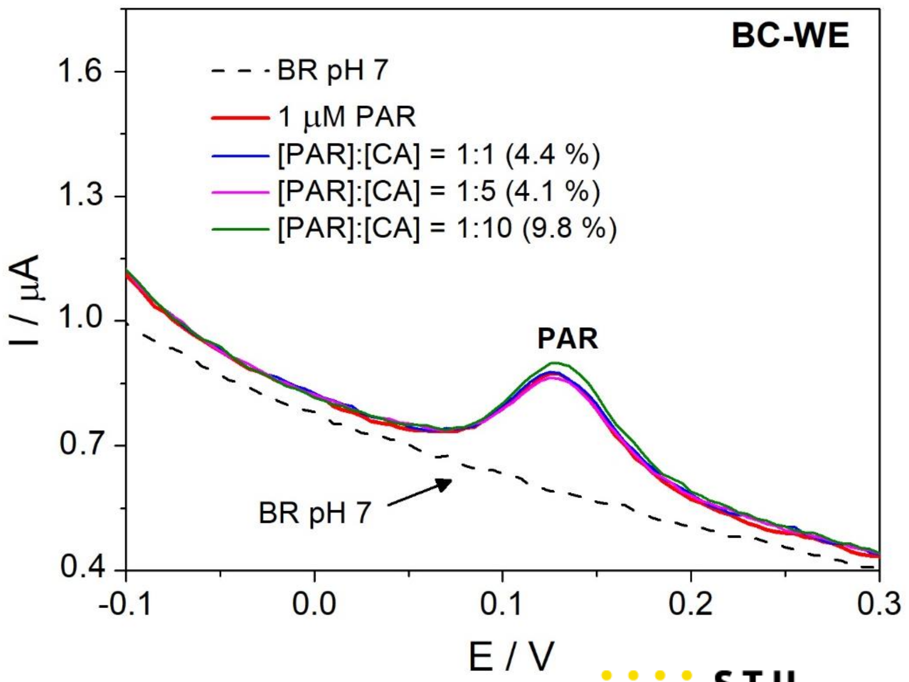
Interference study

<u>1 µM of PAR (fixed amount) in BR buffer pH 7 using DPAdSV at BC-WE</u>:

- 100-fold excess of Na^{+}, K^{+}, Mg^{2+}, Zn^{2+}, Fe^{3+}, NO_3^{-}, PO_4^{3-} and SO_4^{2-} – no effect on the peak current of PAR
- 50-fold excess of glucose, fructose, sucrose, cellulose and starch – minor effect (the signal change of PAR < 10 %)
- 10-fold excess of caffeine (CAF), ascorbic acid (AA) and citric acid (CA) – minor to negligible effect
- satisfactory selectivity of the developed methodology in pharmaceutical analysis







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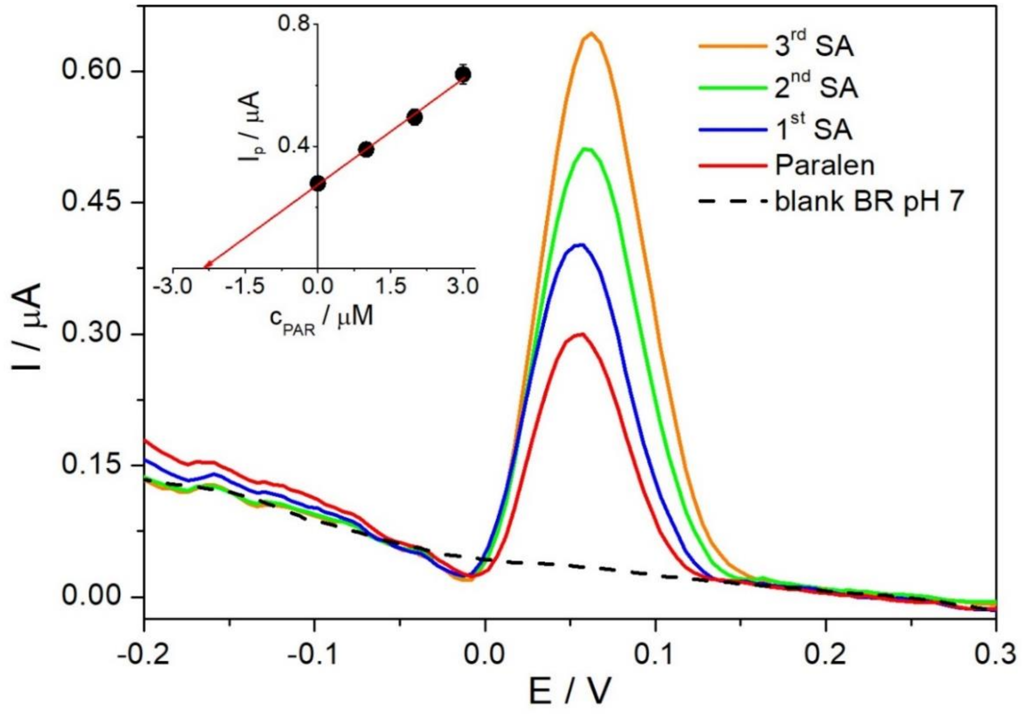
Analysis of pharmaceutical formulations

Products	Declared content (mg)	Determined amount (mg)	Recovery (%)
Ataralgin®	325	313 ± 13	96.3
Panadol®	500	497 ± 10	99.4
Paralen®	500	480 ± 23	95.8



DPAdSV records for determination of PAR in pharmaceutical dosage *Paralen®* in BR buffer pH 7 at **BC-WE** using the standard addition method.

Operating parameters:
modulation time 100 ms
modulation amplitude 100 mV
step potential 5 mV
accumulation potential 0 V
accumulation time 300 s

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Comparison with other electrochemical sensors for PAR determination based on electrode materials prepared from biomass resources

Electrochemical sensor	Biomass resource	Processing of biomass	Activation step	Technique	Linear range (μM)	LOD (nM)	Analyzed sample	Reference
N/Fe–C/GCE	pork liver	calcination at 450 °C for 2 h and at 800 °C for 2 h (1 °C min^{-1})	KOH	DPV	0.5 – 220	79	serum	Zhou et al. (2017)
ZKAKC/GCE	kelp	carbonization at 700 °C for 3 h (10 °C min^{-1})	$ZnCl_2$ KOH	DPV	0.01 – 20	4	urine	Kim et al. (2018)
ZnO-MoO_3-C/GCE	mushrooms	calcination at 550 °C for 3 h (2 °C min^{-1})	–	DPV	2.5 – 2000	114	serum, tablets	Liu et al. (2021)
AuNCs/BC/GCE	*Soulangeana sepals*	carbonization at 800 °C for 2 h	KOH	DPAdSV	0.003 – 50	1	serum	Yu et al. (2022)
(N-SC/-CD-MOFs)/GCE	*Soulangeana sepals*	carbonization at 800 °C for 2 h	KOH	DPAdSV	1.0 – 30.0	0.3	lake water	Yu et al. (2023)
Screen-printed BC-WE	40% corn 60% wood	pyrolysis at 470 °C for 25 min	–	DPAdSV	0.1 – 10	20	tablets	Švorc et al. (2024)

Abbreviations: AuNCs/BC/GCE – glassy carbon electrode modified with biochar decorated with gold nanoclusters, BC-WE – biochar-modified carbon electrodes, DPAdSV – differential pulse adsorptive stripping voltammetry, DPV – differential pulse voltammetry, N/Fe–C/GCE – glassy carbon electrode modified with iron-nitrogen co-doped porous carbon, (N-SC/-CD-MOFs)/GCE – glassy carbon electrode modified with nitrogen-doped biochar/ß-cyclodextrin-metalorganic frameworks, ZKAKC/GCE – glassy carbon electrode modified with $ZnCl_2$-KOH activated kelp carbon, ZnO-MoO_3-C/GCE – glassy carbon electrode modified with nanocomposite electrode with ZnO-MoO_3 and biochar

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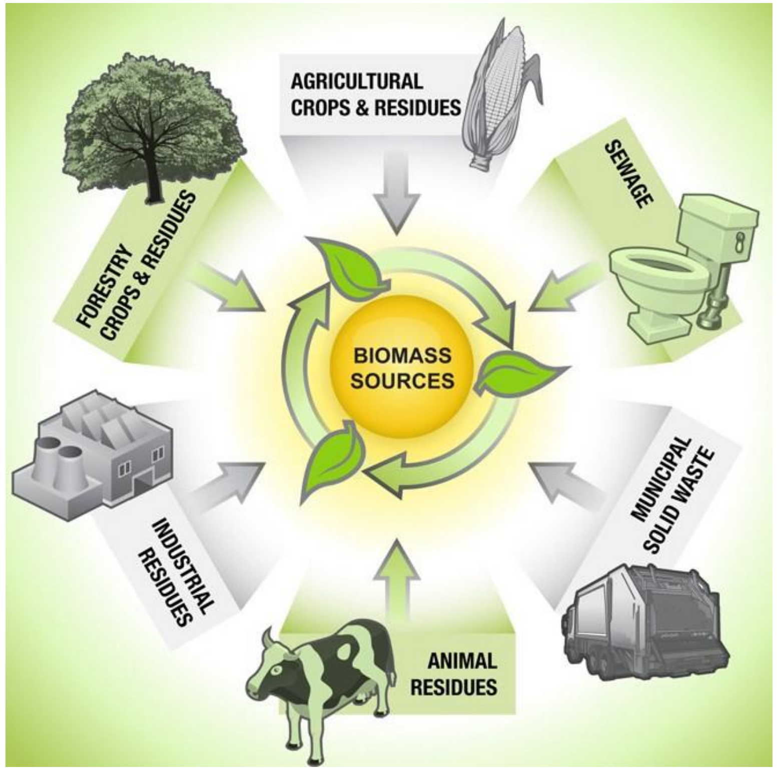
Conclusions and perspectives

- **Biochar** – perspective electrode material for screen-printed electrochemical sensors.
- Beneficial properties of biochar → use in electroanalysis.
- Novel and reliable electrochemical sensing platform for determination of paracetamol in pharmaceutical formulations.

Perspectives:

- Structural and morphological properties *versus* electrochemical properties.

  Crucial parameters:
  - biomass (origin, composition),
  - pyrolysis conditions (temperature, heating rate, time),
  - heterogeneity,
  - surface functionalization.



- Biochar-based sensors in flow and batch systems.

Thank you for your attention ☺

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